



ARL-TN-0748 • APR 2016



Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB)

by Edward FC Byrd

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.



Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB)

by Edward FC Byrd

Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) April 2016		2. REPORT TYPE Technical Note		3. DATES COVERED (From - To) 1 November 2015–31 January 2016	
4. TITLE AND SUBTITLE Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Edward FC Byrd				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Army Research Laboratory ATTN: RDRL-WML-B Aberdeen Proving Ground, MD 21005-5069				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TN-0748	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Using a series of scripts developed by the US Army Research Laboratory, written to dramatically simplify the computation of crystalline density and heat of formation, the performance properties were evaluated for the 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB) notional energetic materials. A qualitative estimation of the impact sensitivities has also been calculated. This report outlines the procedures used to generate this information and includes Cheetah calculations using the predicted crystalline density and heat of formation.					
15. SUBJECT TERMS computational toolbox, script, crystalline density, heat of formation, impact sensitivity, energetic materials					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON Edward FC Byrd
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 410-306-0729

Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Results and Discussion	1
3. Conclusion	6
4. References	7
List of Symbols, Abbreviations, and Acronyms	8
Distribution List	9

List of Figures

Fig. 1	Optimized structure of a) AMDNNM , b) BAFDAONAB , and c) BNFDAONAB.....	2
Fig. 2	Electrostatic potential map of AMDNNM: a) without and b) with molecule overlay	3
Fig. 3	Electrostatic potential map of BAFDAONAB: a) without and b) with molecule overlay	4
Fig. 4	Electrostatic potential map of BNFDAONAB: a) without and b) with molecule overlay	5

List of Tables

Table 1	Computed heats of formation and crystalline densities for AMDNNM, BAFDAONAB, and BNFDAONAB	3
Table 2	Cheetah-predicted properties for AMDNNM, BAFDAONAB, and BNFDAONAB.....	5

Acknowledgments

Dr Betsy Rice and Jennifer J Hare are acknowledged for their efforts in the original coding of the neutral heat of formation and Education Data Analysis Tool (EDAT) tools, respectively. Dr Anthony Yau is acknowledged for his work in revising the EDAT code. Dr James Ianni (Applications Engineer with Lockheed Martin, contractor to the US Army Research Laboratory Department of Defense Supercomputing Resource Center [ARL DSRC]) is acknowledged for his “gsubmit” script, initially written for the ARL DSRC. All computations were performed at the ARL DSRC, Aberdeen Proving Ground, MD. Calculations were performed at the behest of Dr David Boruta (Naval Surface Warfare Center–Indian Head, MD).

INTENTIONALLY LEFT BLANK.

1. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties including heats of formation,^{1,2} densities,^{3,4} and impact sensitivity⁵ of energetic materials and have begun growing advanced synthesis capabilities to realize notional materials. This dual capability allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. For an in-depth explanation of the different theoretical methods employed herein, please refer to previous works.^{6,7} This technical note will detail theoretical predictions of heat of formation, density, sensitivity, and performance for the 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB) notional energetic materials.⁸

2. Results and Discussion

The properties of AMDNNM, BAFDAONAB, and BNFDAONAB (Figs. 1a–1c) were predicted using ARL tools.⁷ To estimate the impact sensitivities, the electrostatic maps on the 0.001 isosurfaces were generated with the scalar range of the electrostatic surface potential (ESP) ranging from -0.05 to 0.075 . For this visualization methodology, regions of large positive charge (i.e., electron-deficient regions, labeled in red) over the backbone of the structure tend to indicate increased sensitivity.

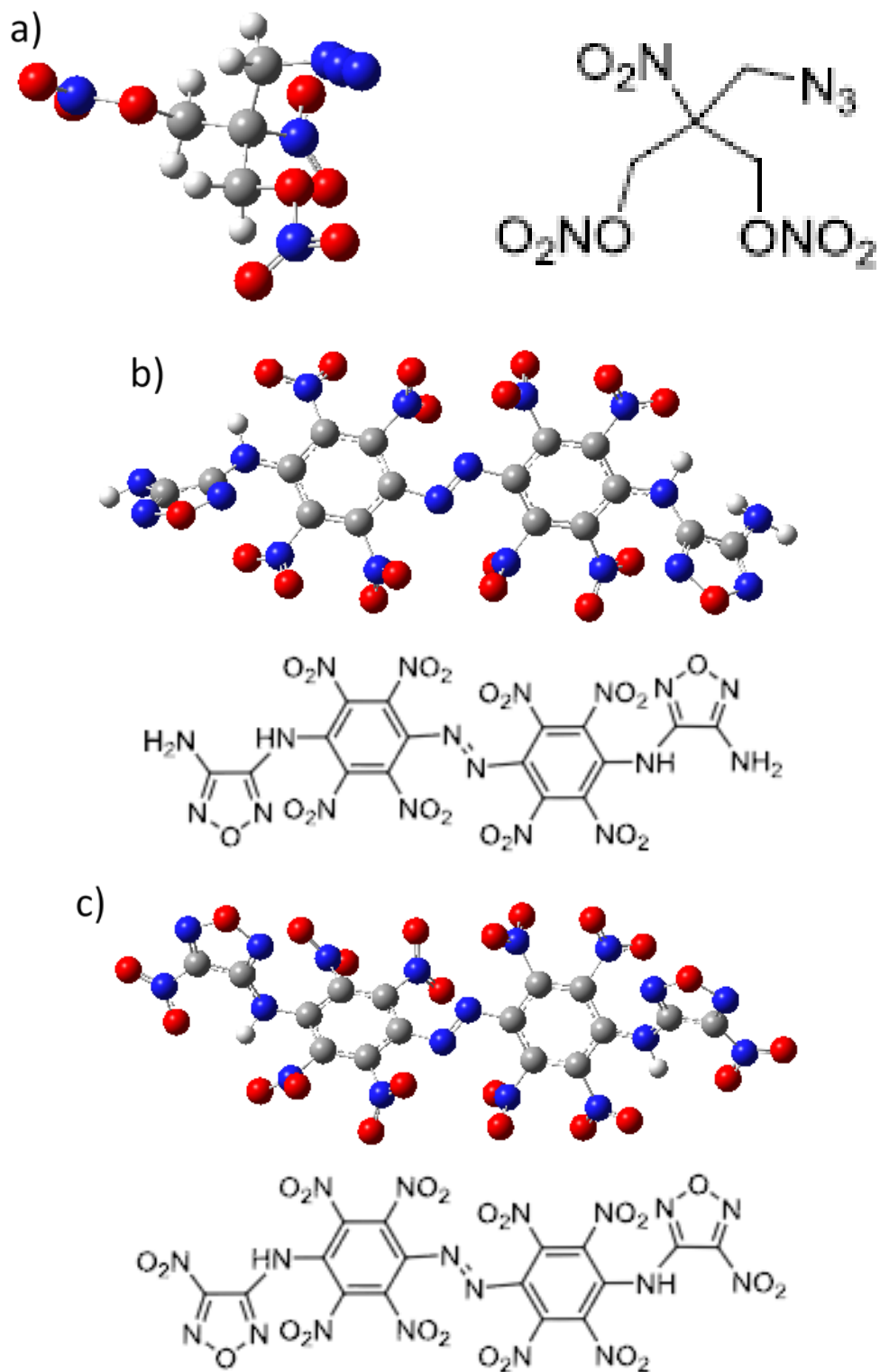


Fig. 1 Optimized structure of a) AMDNNM , b) BAFDAONAB , and c) BNFDAONAB

The computed heats of formation and crystalline densities for these molecules are presented in Table 1.

Table 1 Computed heats of formation and crystalline densities for AMDNNM, BAFDAONAB, and BNFDAONAB

Molecule	Solid phase heat of formation (kcal/mol)	Density (g/cm ³)
AMDNNM	1.182	1.720
BAFDAONAB	175.518	1.898
BNFDAONAB	180.912	1.934

Additionally, we plot the ESP maps for AMDNNM (Figs. 2a and 2b), BAFDAONAB (Figs. 3a and 3b), and BNFDAONAB (Figs. 4a and 4b) with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify AMDNNM as moderately sensitive, BAFDAONAB as slightly sensitive to insensitive, and BNFDAONAB as sensitive. That said, chemist intuition would classify AMDNNM as likely to be very sensitive. It would be of interest to compare the experimental with the predicted results for AMDNNM. We performed Cheetah 8.0 calculations⁹ to predict the performance parameters using the predicted heats of formation and densities. At the Chapman-Jouguet point, Cheetah yields the values shown in Table 2.

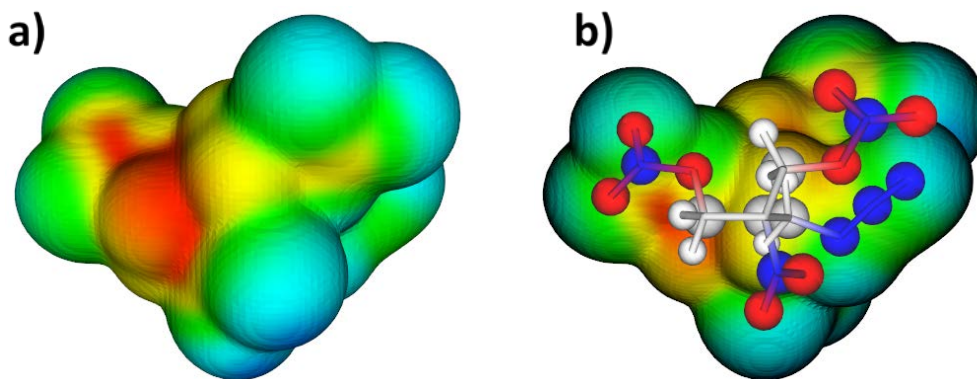


Fig. 2 Electrostatic potential map of AMDNNM: a) without and b) with molecule overlay

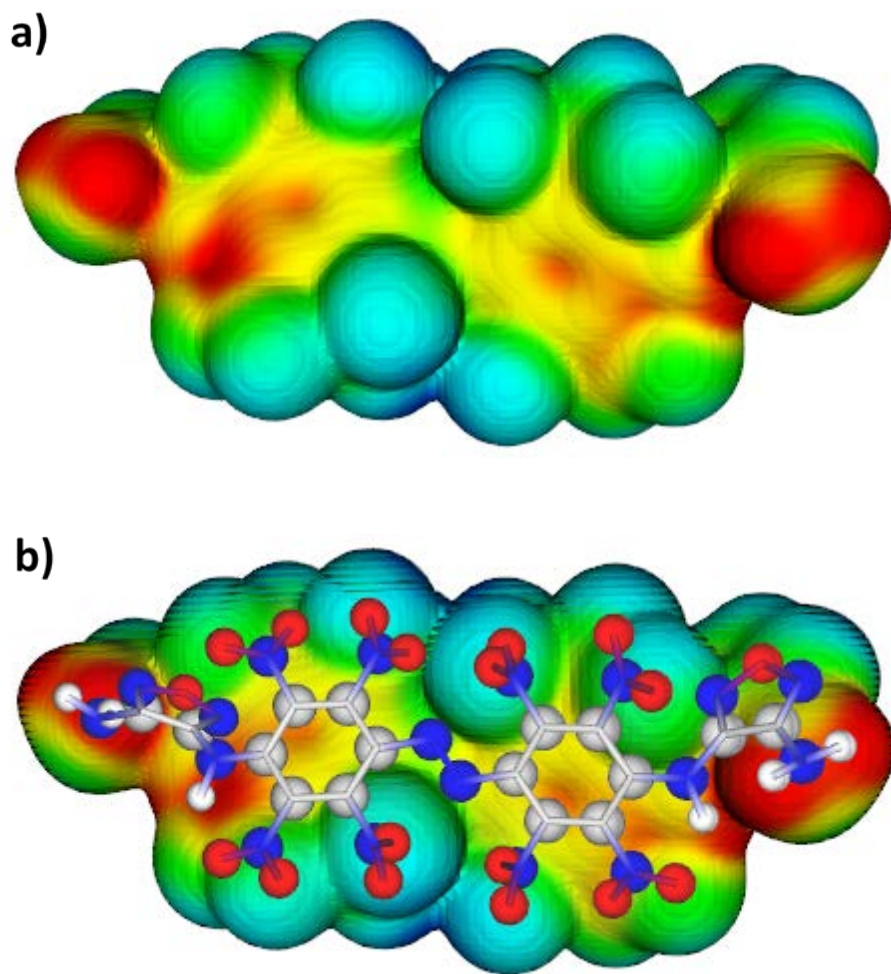


Fig. 3 Electrostatic potential map of BAFDAONAB: a) without and b) with molecule overlay

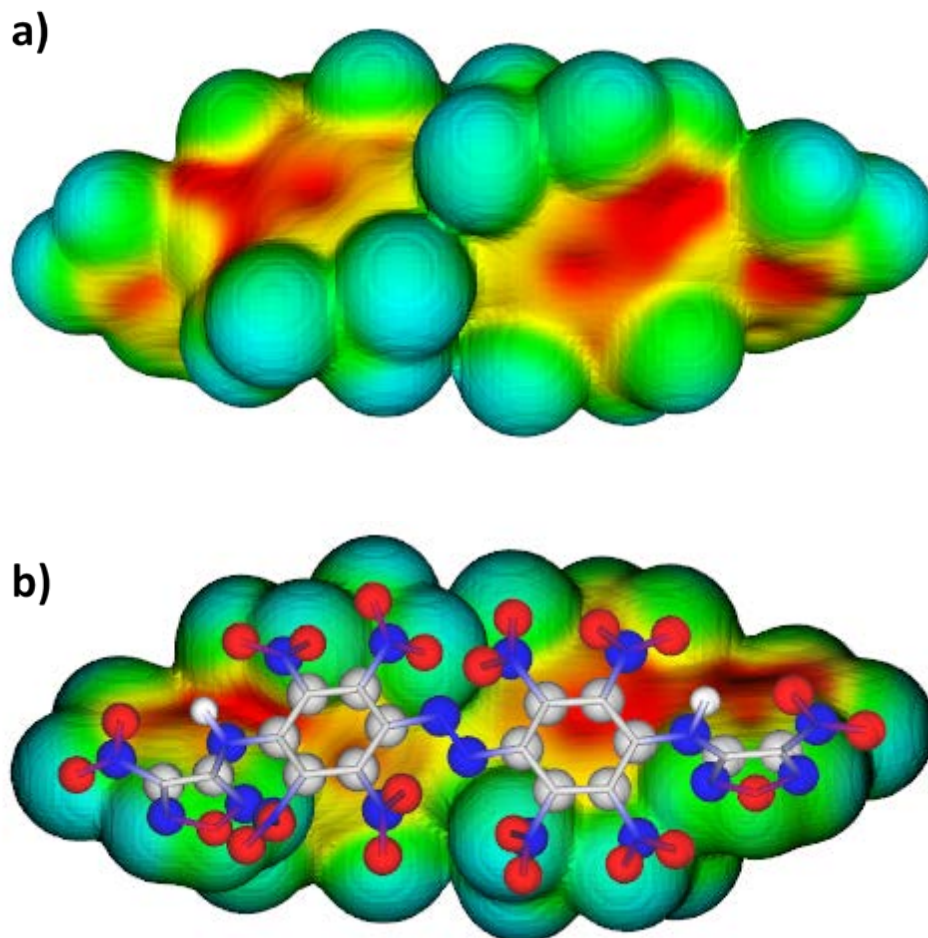


Fig. 4 Electrostatic potential map of BNFDAONAB: a) without and b) with molecule overlay

Table 2 Cheetah-predicted properties for AMDNNM, BAFDAONAB, and BNFDAONAB

Molecule	Pressure (GPa)	Shock velocity (km/s)	Temperature (K)	Total energy of detonation (TNT equivalent) (per cm ³)	Total energy of detonation (TNT equivalent) (per g)
AMDNNM	29.348	8.275	3,663.1	1.349	1.297
BAFDAONAB	31.278	8.545	3,665.6	1.339	1.167
BNFDAONAB	35.442	9.011	4,116.3	1.435	1.227

Note: TNT = trinitrotoluene.

3. Conclusion

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the AMDNNM, BAFDAONAB, and BNFDAONAB molecules. Using this predicted data, we then ran Cheetah calculations to predict the performance of these materials. Additionally, we predicted the qualitative impact sensitivities of these compounds using electrostatic potential maps. This information has been transitioned back to the requesting synthetic chemist, Dr David Boruta of Naval Surface Warfare Center–Indian Head.

4. References

1. Byrd EFC, Rice BM. Improved prediction of heats of formation of energetic materials using quantum mechanical calculations. *J Phys Chem A*. 2006;110(3):1005–1013.
2. Byrd EFC, Rice BM. A comparison of methods to predict solid phase heats of formation of molecular energetic salts. *J Phys Chem A*. 2009;113(1):345–352.
3. Rice BM, Hare JJ, Byrd EFC. Accurate predictions of crystal densities using quantum mechanical molecular volumes. *J Phys Chem A*. 2007;111(42):10874–10879.
4. Rice BM, Byrd EFC. Evaluation of electrostatic descriptors for predicting crystalline density. *J Comp Chem*. 2013;34(25):2146–2151.
5. Rice BM, Hare JJ. A quantum mechanical investigation of the relation between impact sensitivity and the charge distribution in energetic molecules. *J Phys Chem A*. 2002;106(9):1770–1783.
6. Byrd EFC. Theoretical prediction of the heat of formation, density, and relative sensitivity for 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2015 Apr. Report No: ARL-TN-0680.
7. Byrd EFC. On the failure of correlating partitioned electrostatic surface potentials using Bader's atoms-in-molecules theory to impact sensitivities. Aberdeen Proving Ground (MD): Army Research Laboratory (US); 2013 Sep. Report No: ARL-TR-6206.
8. Boruta DT. Naval Surface Warfare Center, Indian Head, MD. Private communications, 2015 Nov and 2016 Jan.
9. Bastea S, Fried LE, Glaeseman KR, Howard WM, Kuo IFW, Souers PC, Vitello, PA. Cheetah 8.0 thermochemical code. Livermore (CA): Lawrence Livermore National Laboratory Energetic Materials Center; 2015.

List of Symbols, Abbreviations, and Acronyms

AMDNNM	2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate
ARL	US Army Research Laboratory
BAFDAONAB	bis-aminofurazan diamino-octanitro-azobenzene
BNFDAONAB	bis-nitrofurazan diamino-octanitro-azobenzene
ESP	electrostatic surface potential
TNT	trinitrotoluene

1 DEFENSE TECHNICAL
(PDF) INFORMATION CTR
DTIC OCA

2 DIRECTOR
(PDF) US ARMY RESEARCH LAB
RDRL CIO LL
IMAL HRA MAIL & RECORDS
MGMT

1 GOVT PRINTG OFC
(PDF) A MALHOTRA

1 NAVAL RSRCH LAB
(PDF) TECH LIB

1 US ARMY ARDEC
(PDF) A DISTASIO

1 US ARMY ARDEC
(PDF) S NICOLICH

18 DIR USARL
(PDF) RDRL CIN S
K RENARD
RDRL WM
D LYON
B FORCH
J ZABINSKI
RDRL WML
M ZOLTOSKI
RDRL WML A
W OBERLE
RDRL WML B
N TRIVEDI
J MORRIS
B RICE
E BYRD
RDRL WML C
S AUBERT
J SABATINI
J BANNING
RDRL WML D
R BEYER
RDRL WML E
P WEINACHT
RDRL WML G
W DRYSDALE
RDRL WML H
J NEWILL
RDRL WMP G
R EHLERS

INTENTIONALLY LEFT BLANK.